

# Observations of organic species and atmospheric ice formation

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**Abstract.** Aerosol particles found in the lower confines of the atmosphere are typically internal mixtures of sulfate, inorganic salts, refractory components, and organic species. The effect these complex combinations have on cloud formation processes remains largely unknown. We have conducted two complementary studies on one important process, the homogeneous formation of ice by small particles. In the first study the freezing of atmospheric aerosol was induced using controlled temperature and humidity conditions. In the second study the chemical composition of the residue from ice crystals in high altitude clouds was analyzed. Here we show that organic components do not partition equally to the ice and aqueous phases. Instead, organic-rich particles preferentially remain unfrozen. These results suggest that emissions of organic species have the potential to influence aerosol-cold cloud interactions and climate.

## Introduction

The term 'indirect effect' has been applied to the impact of particles on climate through their complex interaction with clouds. Indirect radiative forcing is subdivided into effects attributed to warm clouds, which remain entirely unfrozen, and those that contain ice crystals. Warm cloud processes are the better understood, including observed links between aerosol, cloud drop number, and precipitation [Brenquist, 1997; Baker, 2000]. Although ice formation can be an important step in precipitation, this aspect of the indirect effect remains largely unexplored. IPCC [2001] notes that anthropogenic effects on ice and mixed-phase clouds, and the related climatic impact, also remain unknown. A number of factors are responsible, among them the high altitude of frozen clouds, a lack of appropriate instruments, and uncertain processes such as

ice multiplication and scavenging. Because of these uncertainties, atmospheric ice formation, specifically cirrus cloud formation, remains a difficult process to model. The state of knowledge of ice nucleation currently hinders our ability to understand ice cloud formation and the humidity of the upper troposphere and stratosphere.

Primary ice formation proceeds via two distinct pathways, homogeneous or heterogeneous freezing. Both are climatically important. Homogeneous nucleation refers to the spontaneous formation of the ice phase within an aqueous matrix. Water droplets found in the atmosphere do not homogeneously freeze at 0° C due to a kinetic barrier to crystal formation. 'Supercooling' to approximately -38° C is required before the spontaneous formation of ice becomes probable [Pruppacher and Klett, 1997]. Solutes commonly associated with atmospheric aerosol have been shown to further increase the amount of supercooling [Koop *et al.*, 2000]. At temperatures warmer than about -38° C, or at relative humidities lower than a few percent below water saturation, heterogeneous ice formation is initiated by the presence of solid particles with an appropriate structure, known as ice nuclei (IN) [AAN, 1977]. The majority of particles found in the troposphere do not appear to contain IN, however [Sassen and Dodd, 1988]. The semi-volatile nature of the large reservoir of particles able to undergo homogeneous freezing has precluded extensive study using traditional EM techniques that take place *in vacuo* [Heintzenberg *et al.*, 1996]. Only recently have experiments been performed to understand volatile and semi-volatile components of particles that form ice in the atmosphere [DeMott *et al.*, 2003]. The focus of this work is to describe two studies of aerosol that homogeneously freezes using a single particle laser ablation technique that is sensitive to both refractory and non-refractory aerosol components [Cziczo *et al.*, 2003].

## Field Studies

The first set of experiments was conducted during November 2001 at Storm Peak Laboratory (SPL) in northern Colorado. SPL is equipped with extensive particle monitoring equipment. Further, the remote location and high elevation, 3200 meters above sea level, permitted sampling from the clean troposphere [Borys and Wetzel, 1997] in which the majority of ice cloud formation takes place. Aerosol was subjected to controlled temperature and saturation conditions using the Colorado State University Continuous Flow Diffusion Chamber (CFDC), described previously [DeMott *et al.*, 2003]. Briefly, the CFDC focuses aerosol between

two ice-coated walls held at different temperatures. The temperature gradient between the walls and a sheath flow are used to limit aerosol exposure to constant temperature ( $\pm 0.7^\circ\text{C}$ ) and relative humidity ( $\pm 0.7\%$  with respect to water) conditions. Particles that nucleated ice were optically counted and separated from those that did not freeze using a counterflow virtual impactor (CVI) [Cziczo *et al.*, 2003]. The percentage of aerosol nucleating ice was calculated by comparing the number of crystals formed under given CFDC conditions to the total number of atmosphere particles larger than 100 nm diameter, from which the majority of ice formation originates [Chen *et al.*, 1998], measured by scanning mobility particle sizing (SMPS-TSI). Figure 1 shows a profile of atmospheric ice formation, illustrating the dearth of IN and the switch from heterogeneous to homogeneous freezing. This signature of freezing has been previously presented [Cziczo *et al.*, 2003; DeMott *et al.*, 2003] with an emphasis on particle composition changes between the two modes of freezing and the effect of large-scale meteorology. It is used here to examine compositional differences throughout the entire homogeneous freezing regime. The onset of homogenous freezing was observed to occur a few percent sub-saturated with respect to water, consistent with laboratory studies of sulfate aerosol [Chen *et al.*, 2000]. The fraction of particles nucleating ice increased by several orders of magnitude as the humidity was raised past water saturation.

Chemical composition, after evaporation of condensed-phase water, was determined using the NOAA Aeronomy Lab Particle Analysis by Laser Mass Spectrometry (PALMS) instrument [Cziczo *et al.*, 2003]. Aerosol particles are drawn into PALMS using a vacuum. Particles are detected using a YAG laser ( $\lambda = 532\text{ nm}$ ) with scattered light used to trigger an excimer laser ( $\lambda = 193\text{ nm}$ ) that both ablates and ionizes components. A complete positive or negative mass spectrum is obtained on a particle-by-particle basis using a time-of-flight mass spectrometer. The lower particle diameter for which mass spectra were resolved for these studies was between 0.15 and 0.3  $\mu\text{m}$ . Negative polarity single particle mass spectra acquired at increasing saturation, and therefore fraction of particles freezing, are presented in Figure 2. Nearly all particles contained sulfate and/or organic material, consistent with the composition of the majority of free tropospheric aerosol [Murphy *et al.*, 1998]. The signal attributed to sulfate and organic species did not remain constant as the fraction of particles nucleating ice increased, however (Figure 3). Those particles that froze most readily (i.e., at the lowest saturation for a given temperature) exhibited minimal or no signal attributed to organic components whereas

particles with large organic signal required higher saturation conditions. Previous studies using PALMS show that the negative ion organic signal typically represents a lower limit for the concentration of organic material in the particle [Middlebrook *et al.*, 1997].

A second set of experiments was conducted by flying the same mass spectrometer aboard a NASA WB-57F aircraft. The study occurred during July 2002 as part of the Cirrus Regional Study of Tropical Anvils and Cirrus Layers - Florida Area Cirrus Experiment (CRYSTAL-FACE) [Jensen *et al.*, 2004]. Unlike the ground-based SPL mission the aircraft flights penetrated ice clouds that had resulted from atmospheric freezing. Unlike the CFDC experiments parameters such as initial saturation, temperature, cloud heterogeneity, and size-dependant sedimentation of ice crystals have an unknown impact on the data. A CVI inlet was used to separate cloud elements from ~5-22 micrometers diameter from larger crystals and unfrozen particles [Cziczo *et al.*, 2004]. Mass spectra of ice residue were taken on a crystal-by-crystal basis after condensed-phase water was evaporated. Ice crystals were sampled ~80% of the in-cloud period with the inlet switched to a mode that retained small unfrozen particles within clouds, termed 'interstitial aerosol', for the remaining time. This allowed organic signal from the ice residue to be compared to the average value for the interstitial aerosol as a function of the fraction of the total aerosol that froze (Figure 4). The later quantity was derived by comparing the number density of unfrozen ambient particles, using the FCAS instrument [Jonsson *et al.*, 1995], to the concentration of ice crystals, using the CAPS instrument [Baumgardner *et al.*, 2002]. Consistent with the ground-based SPL study, minimal organic signal was detected when less than 1% of particles nucleated ice. The organic signal of the unfrozen interstitial particles remained higher than the ice residue regardless of the fraction of particles freezing.

## Discussion and Conclusions

These data do not allow us to definitively state that organics cause a suppression of ice formation. Instead, we conclude that particles with high organic signal are not efficient at ice nucleation. We note that these complementary studies, one using controlled temperature and saturation conditions and the other from within atmospheric ice clouds, both exhibit the same behavior. Since it has been shown that single particle mass spectrometry can detect a wide range of species and abundances [Murphy *et al.*, 1998], and we find no quantity other than organic signal that co-varies in the same manner to offer an alternative explanation, we consider this

association important. Furthermore, although we have not attempted to observe a direct link between organics and a perturbation of ice cloud properties, we believe it is important to note that parameters such as cloud density and dissipation may be affected by these species. It follows that aerosol particles, for which precipitation is the major removal mechanism, may have a composition-dependent lifetime. Related parameters, such as upper tropospheric humidity and precipitation, could also be modified by the presence of organic species and any changes induced in their abundance or distribution by anthropogenic activities.

The unequal partitioning of organics to the ice and aqueous phases draws forth two resulting questions that require further study. First, it is uncertain by what process(es) organic components may affect ice formation. *Koop et al.* [2000] have proposed that nucleation per unit volume is solely a function of water activity. It is plausible that this theory is correct but that organic components create hygroscopicity differences between particles that affect water uptake [*Rudich et al.*, 2003]. Disparate water uptake between pristine sulfate and internally mixed organic/sulfate aerosols would lead to differences in particle dilution, volume, and, ultimately, freezing point. Alternately, organics may induce kinetic effects, as would be the case with a surface coating, which are not accounted for by *Koop et al.* *Tabazadeh et al.* [2002] have theorized that homogenous ice nucleation does not occur within the bulk but rather at a particle surface. An organic surface component would thus affect surface nucleation, but it remains uncertain how prevalent such coatings are in the atmosphere [*IPCC*, 2001]. Lastly, organics may act in a manner not previously considered important for the atmosphere. *Yeh and Feeney* [1996] have suggested several mechanisms by which antifreeze proteins (AFPs), such as those found in polar fish that survive freezing conditions, inhibit bulk ice formation. For example, AFPs have been shown to bind to and inhibit ice crystal growth. It is plausible that atmospheric aerosols contain organic molecules with similar properties and similar results. Laboratory studies are required to elucidate the correct mechanism. Second, the speciation of the organics involved remains unknown. Laser ablation mass spectrometry causes extensive fragmentation of organic components making identification of precursor species difficult [*Middlebrook et al.*, 1997]. Laboratory studies have not shown significant supercooling effects for sulfate/dicarboxylic acid mixes [*Brooks et al.*, 2004]. This is significant because it indicates that some organic components can be emitted to the atmosphere with little or no effect while other species may have a substantial impact.

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## Figure Captions

**Figure 1.** Percentage of aerosol particles in the background atmosphere that nucleated ice as a function of saturation. This figure represents a single experiment, conducted at a temperature of -50° C, but is indicative of all data collected at Storm Peak Laboratory. The discontinuity just under water saturation, at which point the number of particles nucleating ice increased by four orders of magnitude, is due to a change from heterogeneous to predominantly homogeneous freezing. The dashed

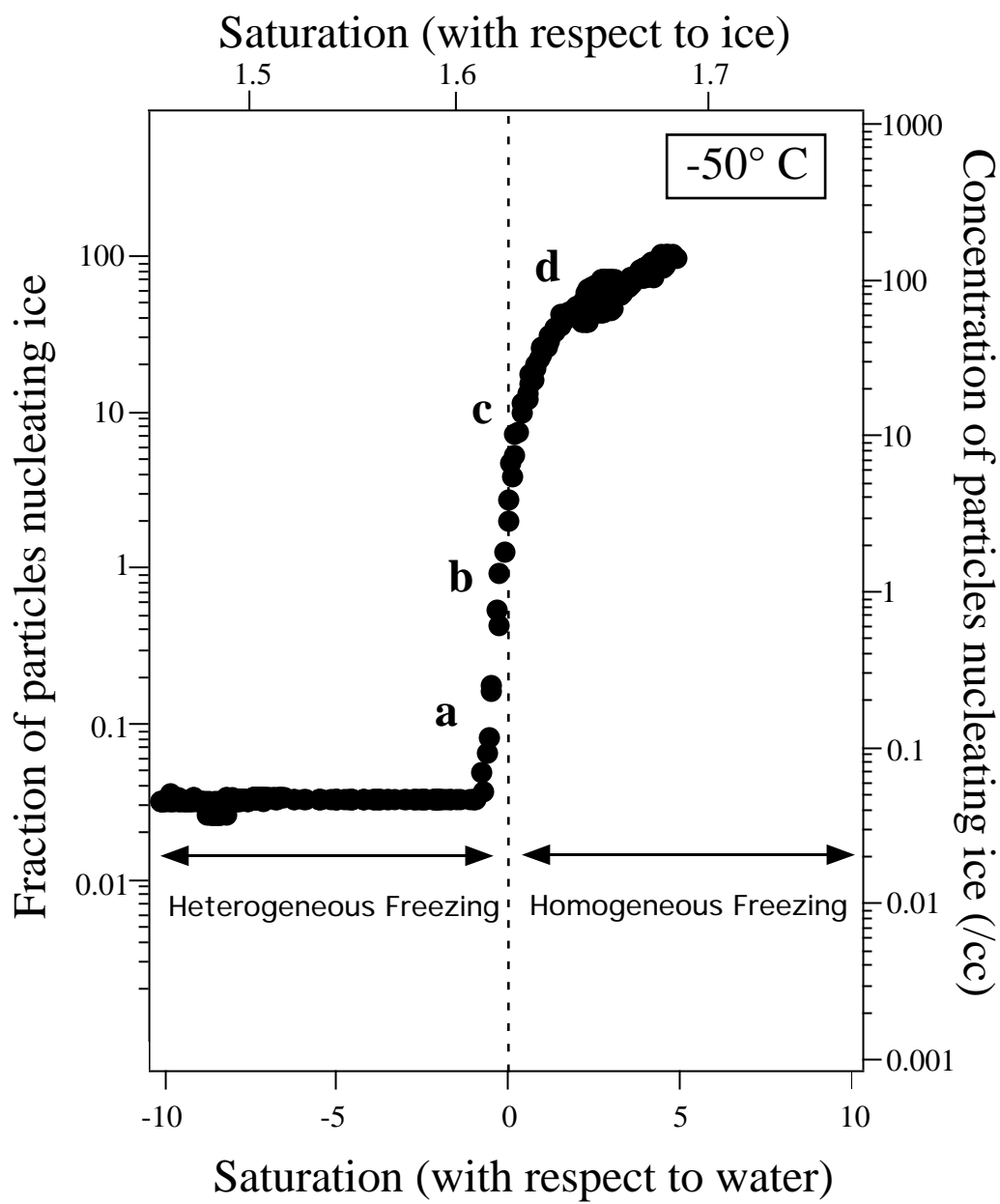
line indicates saturation, with respect to water. Points are certain to  $\pm 1\%$  relative humidity. Conditions at which single particle mass spectra are presented in Figure 2 are indicated by letters a, b, c, and d.

**Figure 2.** Negative ion mass spectra of single particles that froze in four homogeneous freezing regimes described in Figure 1. Panels a through d correspond to particles that froze when progressively larger percentages of the background aerosol was nucleating ice. Spectra contain fragments of sulfate and organic species, components of the majority of free tropospheric particles, but the relative presence of organics was observed to decline as the fraction of particles nucleating ice decreased. Notice that no organic components were detected in the particle that froze at the lowest saturation condition.

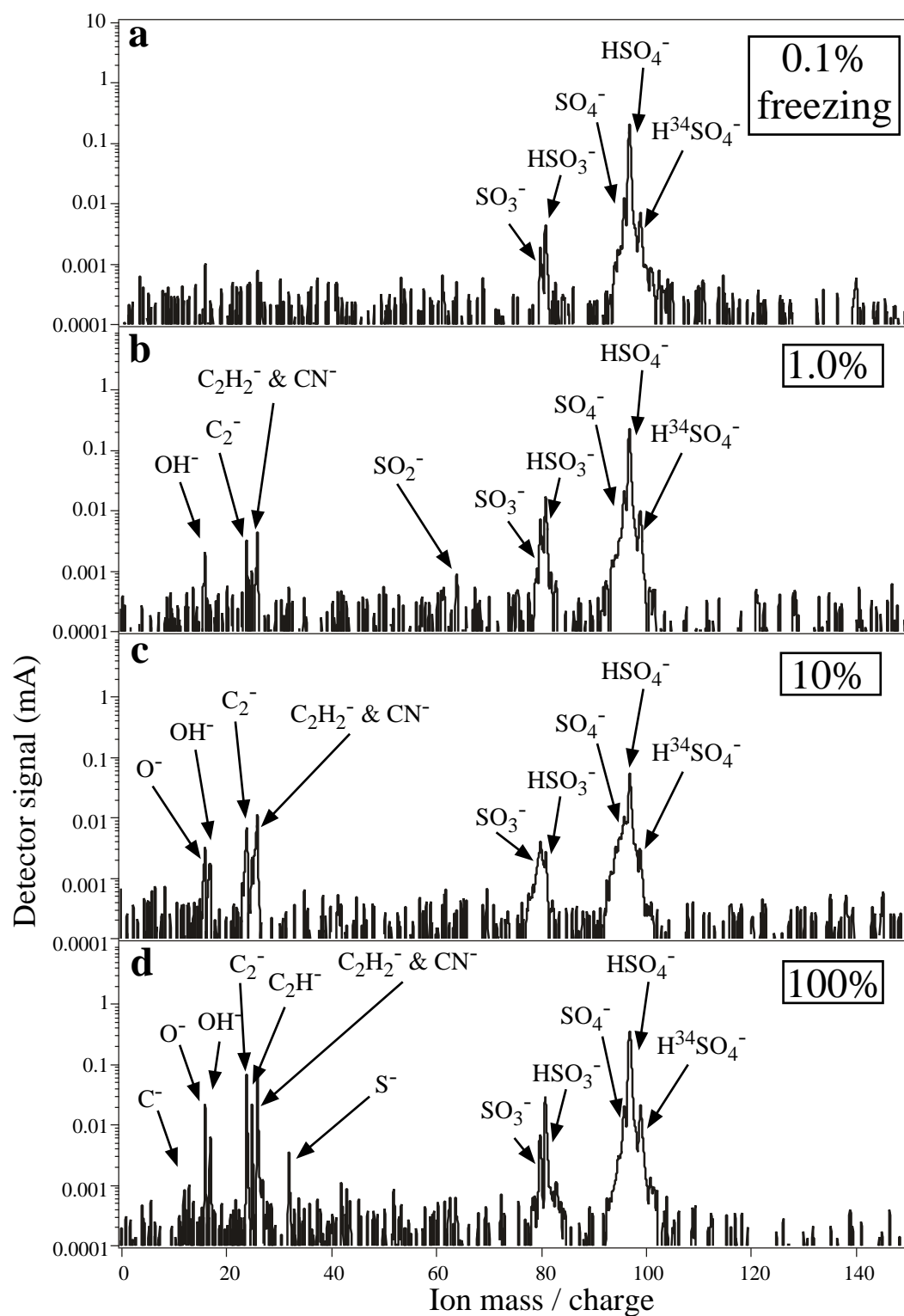
**Figure 3.** Average fraction of signal attributed to sulfate and organic fragments in mass spectra as a function of the percentage of the background aerosol that was nucleating ice. This plot incorporates data from spectra a, b, c, and d from Figure 2, as well as all other data acquired during homogenous ice nucleation studies at Storm Peak Laboratory. When only a small fraction of the background aerosol was nucleating ice those particles had negligible signal attributed to organic fragments. Only when a significant fraction of the aerosol was nucleating ice was organic material found in those particles.

**Figure 4.** Average fraction of signal attributed to organic fragments as a function of the percentage of the background aerosol that was nucleating ice. Data are from all cirrus ice clouds investigated during the CRYSTAL-FACE mission except those that formed during a mineral dust transport event [Cziczo *et al.*, 2004]. Data span cirrus clouds in an altitude range from 11 to 15 km, a temperature from  $-48^{\circ}$  to  $-77^{\circ}$  C, and crystal densities from 0.001 to  $>300$  per  $\text{cm}^3$ . This plot is analogous to Figure 3 but with atmospheric conditions dictating the fraction of particles freezing. Particle composition is observed to change in that when fewer than 1% of the background aerosol was nucleating ice almost no organic fragments were observed in the ice residue. Only when almost all particles were nucleating ice were organics observed at levels approaching the average for those particles that remained unfrozen within clouds, shown as a dashed line.

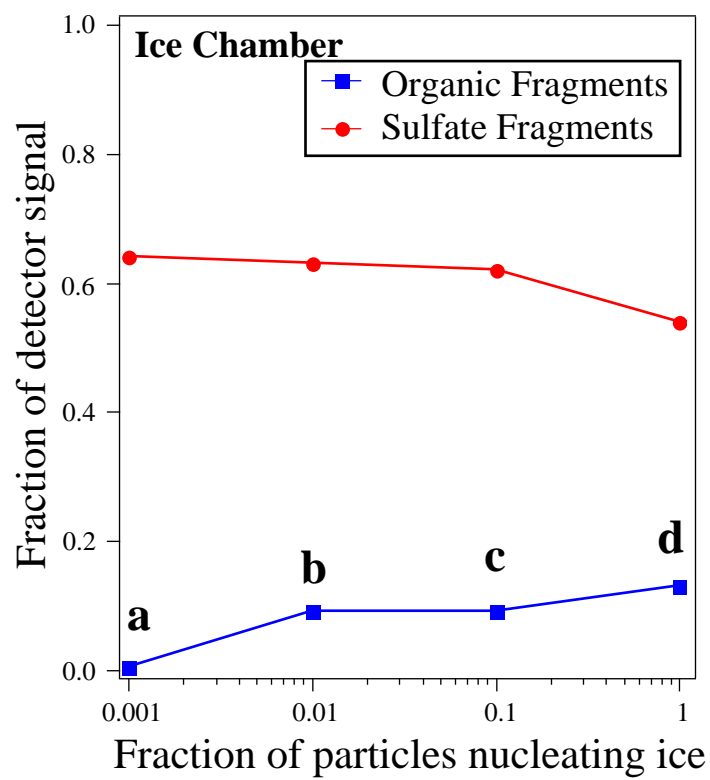




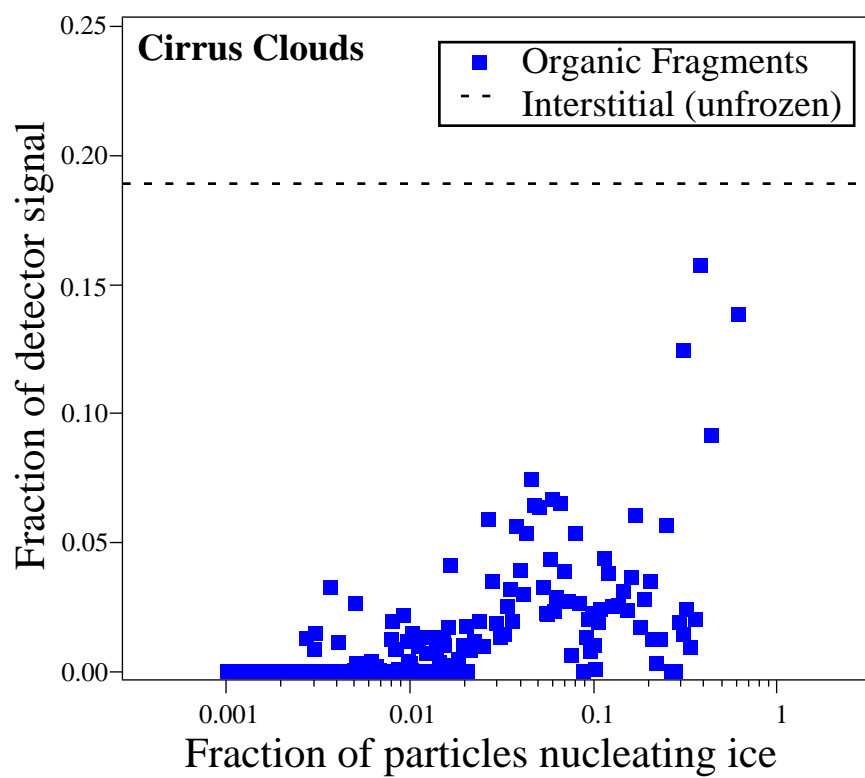
**Figure 1**



**Figure 2**



**Figure 3**



**Figure 4**